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PROCEEDINGS

Biodegradation of Composite Materials

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ABSTRACT

The matrix- and interface-dominated properties of fiber-reinforced polymer composites are known to be sensitive to absorbed moisture. In addition there is a potential for electrochemical corrosion when a carbon fiber composite is mechanically coupled with a metal, such as aluminum, in an aqueous environment. When these composite materials are exposed to aqueous solutions of nutrients, a substantial amount of biological activity is noted on and around the composites. The biological species has been identified as a fungus which is believed to be present in the as-sectioned composite specimens. In light of these observations the question arises of whether composite degradation in humid environments may be assisted or enhanced by biological microorganisms. A study was conducted to investigate this premise wherein biologically-active and sterile composite specimens were immersed in distilled water and a solution of nutrients. The growth of microorganisms was investigated using scanning electron microscopy, and their influence on mechanical property degradation was determined from measurements of interfacial and interlaminar shear strengths on model glass/epoxy composites and unidirectional graphite/epoxy composites, respectively. Mechanical couples of aluminum and a graphite/BMI laminate were also subjected to similar treatments in

aqueous salt solutions, and corrosion of the laminates at the liquid/air interface was compared by SEM.

INTRODUCTION

It has long been known that polymeric materials are susceptible to biological degradation. Examples where such biodegradation is prevalent include pressure-sensitive tapes used for coating gas pipes, polyethylene lids on milk churns, coatings for buried pipes and cables, foams placed in the fuel tanks of military aircraft for explosion prevention, raincoats, liners of gasoline storage tanks, electronic component insulation, and plastic upholstery materials [1]. Most of the literature dealing with biodegradation of polymeric materials is associated with plasticized vinyl systems. The incorporation of plasticizers can enhance the biological attack of otherwise resistant polymers, and the study of microbial deterioration of polymeric formulations has centered mostly on the involvement of microbes with the plasticizer additives [1]. Polyvinyl chloride and other polymers containing suitable nutrients for fungal and bacterial growth require the addition of an antimicrobial agent to prevent growth of microorganisms. Many synthetic polymers are believed to be inert to biological degradation. The reason for this apparent microbial inertness is probably a combination of parameters including chemical bonding, molecular size, molecular configuration, and the ability to absorb water, as well as other undefined factors. Microbial attack can cause polymer property degradation and result in product embrittlement, cracking, and ultimate failure [2].

Microorganisms generally require C, H, C and N, among other elements, as nutrients for survival. Water is also usually required for the microorganisms to function properly. Many of these elements are present to some degree in fiber-reinforced composite materials. However, since synthetic composites to a large extent were thought to be biologically inert, limited work has been done on the biodegradation characteristics of these materials. A material which ordinarily is biologically inert may be susceptible to secondary degradation mechanisms caused or enhanced by biological activity. During their metabolic process microorganisms exude or deposit a variety of waste products which may interact with composite materials in a variety of ways. Possible mechanisms for microbial degradation of polymeric composites include direct attack of the resin by acids or enzymes produced by the microorganisms, blistering as a result of gas evolution within the polymeric phase, cracking due to by-product deposition, and/or

polymeric destabilization by concentrated chlorides or sulfides produced by the microorganisms [3]. Colonization of composite materials by microorganisms has been demonstrated; however, characterization of the degradation has been limited to examinations in optical and scanning electron microscopes, and analyses of mechanical property changes have been limited.

Thermosetting polymers were once considered immune to attack by microorganisms, and their need for protection against microbial attack is only now being realized. Microbial attack has been reported on thermosets such as styrene butadiene rubber (SBR) and urethane foams [4]. In these materials imperfections in the polymer surface can allow the harboring of foreign materials, including water, which then creates an ideal location for microbial growth. Likewise, the microscopically rough surface texture of fiber-reinforced composites may provide similar favorable bonding sites for microorganisms. Blistering and crystal growth on carbon fiber/polymer composites in marine environments has been documented [5]. The blistering is thought to arise from osmosis. Galvanic coupling of these composite specimens with steel and aluminum can result in blistering and the growth of aragonite ($CaCO_3$) crystals [6]. Specimens which were not galvanically coupled with the steel did not display either blistering or crystal formation. The crystal growth was apparently a result of the corrosion process which electrochemically caused a local change in pH near the polymer allowing nucleation and growth of aragonite crystals from the natural sea water. From a limited visual examination, blistering was not apparent on carbon fiber/epoxy composite materials. Further analysis of composite/metal joints and the investigation of possible degradation mechanisms is warranted.

Previous work has shown that inoculation of specimens with a consortia of fungi and bacteria is not necessary to initiate biological activity. A fungus was found to exist in the composite processing and sample preparation laboratory which colonized on the surface of a number of composite materials and their constituents [7]. This fungus may prove to be an ideal species for investigating the biodegradation of composite materials, since it is already present and has shown a proficiency for thriving in composite processing and fabrication environments.

EXPERIMENTAL PROCEDURE

Biodegradation of Composite Material Properties

A variety of materials and properties were tested in this study. Table 1 lists all the specimen sets tested and the different exposure and test conditions. Three to five specimens were tested in each set. All exposures were made in sterilized jars with solutions which had been sterilized prior to testing.

Table 1: Specimens Sets and Test Conditions

Specimen Set	Material	Condition	Sterilized	Days of Exposure
A	AS4/3501-6	Malt Broth	No	121
B	AS4/3501-6	Water	No	113
C	AS4/3501-6	Malt Broth	Yes	120
D	AS4/3501-6	Water	Yes	112
E	AS4/3501-6	Air	No	-
F	Glass Rod/epoxy	Malt Broth	No	91
G	Glass Rod/epoxy	Malt Broth	Yes	91
H	Glass Rod/epoxy	Air	No	-
I	Glass Rod/epoxy	Air	Yes	-
J	BMI/Al	Malt Broth	No	119
K	BMI/Al	Salt Water	No	119
L	BMI/Al	Salt Water	Yes	119

Interlaminar Shear Strength

A unidirectional 20-ply carbon fiber/epoxy composite panel (AS4/3501-6 from Hercules Inc.) was fabricated in an autoclave using the manufacturer's recommended cure procedure. Specimens were sectioned from this panel with a diamond-tipped wet saw blade to an appropriate size for mechanical testing (1.5 in x 0.5 in) and divided into five sets. Two sets, A and B, of as-sectioned specimens were conditioned in separate sterilized jars containing a malt broth solution of nutrients and deionized water, respectively. An additional two sets of specimens, C and D, were sterilized with an ethylene oxide gas

treatment to remove any microbial agents deposited on them as a result of the preparation and sectioning procedures, and similarly conditioned in malt broth and deionized water, respectively. Set E was retained in its as-sectioned condition as a control. After 16 weeks of conditioning, specimen sets B and D were removed and critical point-dried for observation in the scanning electron microscope. After 17 weeks of exposure, specimen sets A and C were also removed and critical point-dried. Following documentation of fungal activity in the SEM, the specimens were tested in three-point flexure with a span-to-depth ratio of 6:1 to promote interlaminar shear failure. Thin rubber pads were placed between the contact pins and specimen to prevent premature surface damage at these locations. Failure modes were noted and interlaminar shear properties were recorded.

Interfacial Shear Strength

Interfacial shear strength was determined from model glass/epoxy composite specimens. A glass rod, 3 mm in diameter, was aligned along the central axis of a rectangular silicone rubber mold, and an epoxy matrix (Epon 828 from Shell Chemical Co. cured with 35 phr Jeffamine D-230 from Texaco Chemical Co.) was cast around it and cured overnight at room temperature. Rectangular slices, approximately 0.25 in thick, were sectioned from this casting perpendicular to the axis of the embedded reinforcing rod and postcured at 80°C for two hours to complete the cure. One set of these specimens (F) and another set (G) - sterilized with ethylene oxide to remove any microbial agents - were placed in separate sterilized jars containing malt broth. A third set of specimens (H) was maintained as a control, while a fourth set (I) was sterilized with ethylene oxide to determine the influence of this treatment on the strength of the interfacial bond. After 13 weeks of exposure, sets F and G were removed from the conditioning environment, and one specimen from each set was critical point-dried for observation in the SEM. The other specimens were dried overnight in a vacuum oven and the interfacial shear strength determined by a "fiber" push-out test, wherein the axial force required to debond the glass rod from the surrounding epoxy was measured in an MTS test machine.

Biodegradation at Composite/Metal Joints

A carbon fiber/bismaleimide composite panel (IM7/5250-4 from Cytek, Inc.) was fabricated using a standard autoclave cure procedure. Rectangular specimens (approximately 3 in x 1 in) were sectioned with a

diamond-tipped wet saw blade and coupled with plastic tabs to aluminum sections of similar dimensions. Two sets of couples, J and K, were placed in sterilized jars containing a malt broth solution of nutrients and deionized salt water (3.5 weight percent NaCl), respectively. A third set, L, was sterilized with ethylene oxide and conditioned in sterile salt water to serve as a control. After 17 weeks of exposure the specimens were removed from their respective solutions and freeze-dried for observation in the SEM.

RESULTS AND DISCUSSION

Biodegradation of Composite Material Properties

Documentation of Fungal Growth

Biological activity was apparent on the as-sectioned composite specimens of set A after only five days of exposure in the malt broth. Observation of these specimens in the SEM revealed extensive fungal growth and interaction of the fungi with the matrix resin of the composite panels. Fungal mycelia were tenaciously attached to the surface of the panels, preferentially within crevices in the rough surface texture (Figure 1). In several locations the mycelia appeared to penetrate the surface of the resin (Figure 2).

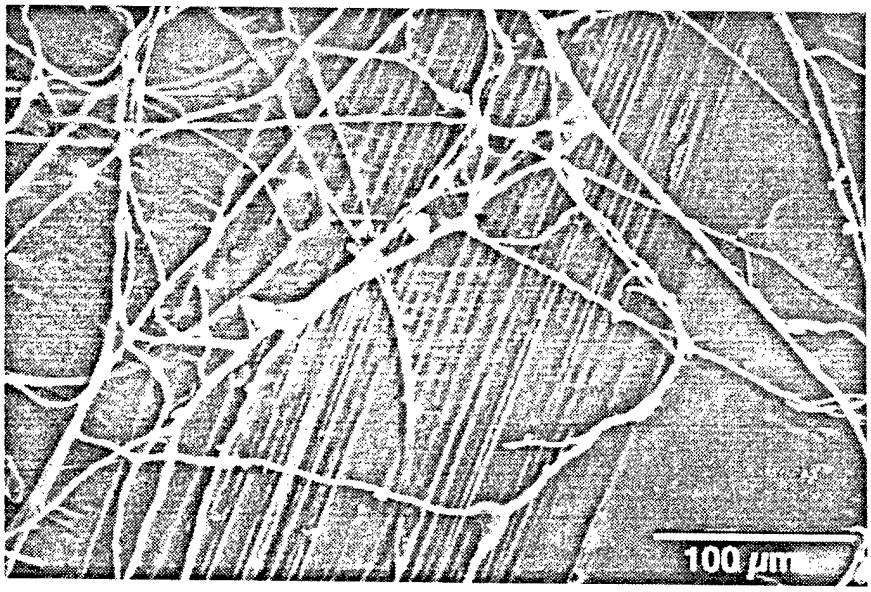

Figure 1: Fungal growth on composite panel which had been placed in a malt broth solution (Set A).

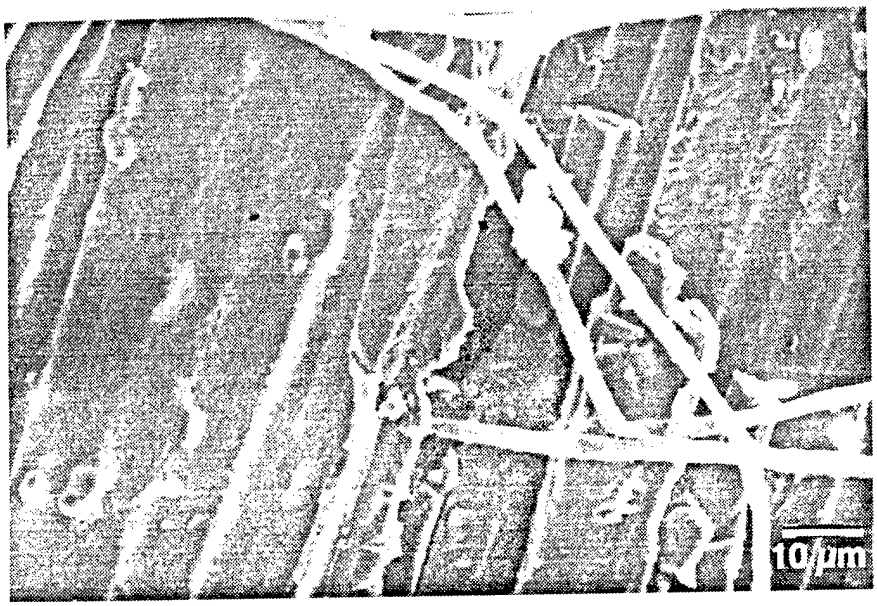

Figure 2: Interaction of fungal mycelia with composite panel (Set A).

Moderate biological activity was visible in the as-sectioned specimens conditioned in water (set B) after approximately 30 days, although SEM examinations of these specimens were required to confirm the existence of the fungi (Figure 3). The overall growth was much less than that observed in the specimens of set A, but was significantly greater than that observed in the sterilized control specimens of sets C and D. Similar interaction of fungal mycelia with the surface roughness characteristics was apparent. It would appear, therefore, that these fungi were able to colonize and grow in the sterile deionized water in the absence of externally-supplied nutrients (such as the malt broth). Consequently, it may be assumed that the composite itself provided the nutritients required for growth, implying that the epoxy matrix and/or carbon fiber is susceptible to microbial attack in the composite's normal working environment.

SEM examination of sterilized specimens conditioned in malt broth and water (sets C and D, respectively) revealed that the presence of fungi was almost nonexistent. The appearance of a few fungal mycelia on some of the specimens could be attributed to cross-contamination of specimens after treatment and prior to the SEM examinations; handling the specimens with tweezers during mounting and coating for SEM observation could have dislodged mycelia from the

as-sectioned specimens and transferred them to the control specimens. Alternatively, fungal activity may not have been completely terminated during the ethylene oxide sterilization process, and some fungal growth may have occurred on these specimens.

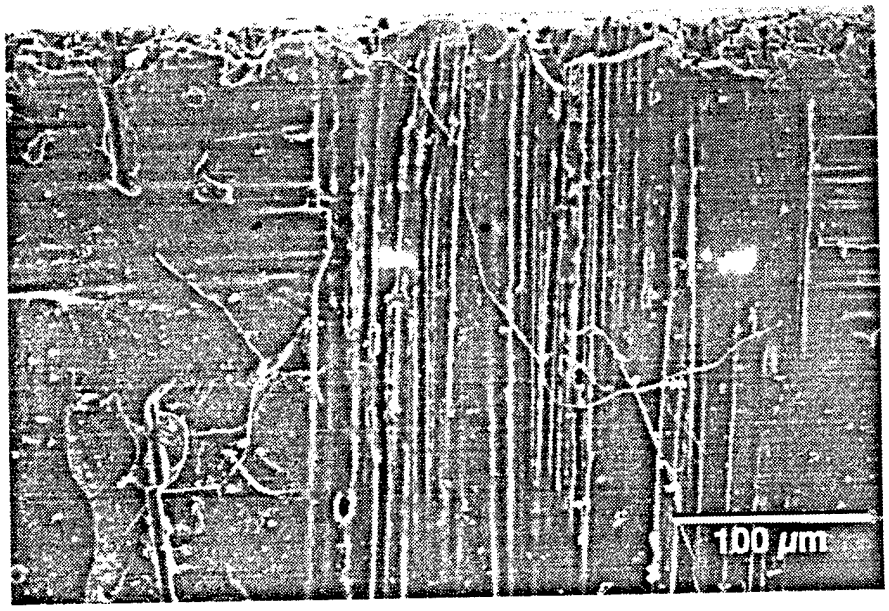

Figure 3: Fungal growth on composite specimen soaked in water (Set B).

Interlaminar Shear Strength

The average interlaminar shear strengths of specimens from sets A-E are listed in Table 2. Failure in all specimens initiated via interlaminar shear near the midplane as confirmed from optical microscopy of polished specimen edges. There was no significant difference in interlaminar shear strength between the panels with biological activity and those which had been sterilized, which suggests that the growth of the fungus on the composite panels did not significantly degrade the resin shear properties. However, other factors may account for the similar shear strengths. The exposure time of the composite sections to the fungus may not have been sufficient enough to degrade material properties. Alternatively, because the majority of the fungal growth occurred on the composite surface, interaction of the fungus may have been limited to the surface plies and edges of the panel. Since this three-point flex test initiates failure at the midplane, the

measured shear strength may not be sensitive to changes in shear properties which occur only at the surface of the panel. The effect of the ethylene oxide treatment on the shear properties is currently unknown as the set of control specimens which were subjected to an ethylene oxide treatment alone were not available for testing.

Table 2: Average Mechanical Properties

Specimen Set	ILSS (ksi)	Interfacial Strength (ksi)
A	15.0	
B	15.6	
C	15.3	
D	15.3	
E	16.3	
F		4.3
G		4.3
H		5.2
I		5.4

Interfacial Shear Strength

The relative shear strengths of the interfacial bond from push-out tests on the model glass/epoxy composites are given in Table 2. Failure was not "clean" as the glass rod fractured prior to being debonded, and the maximum load was used in calculation of the shear strength. The ethylene oxide treatment appears to have improved the shear strength relative to as-sectioned, untreated specimens, while immersion in the malt broth lowered the shear strength of the interfacial bond by approximately 17 percent, even though the specimens were dried prior to testing. In comparing the sterilized and unsterilized specimens conditioned in the malt broth, however, they appear to have equivalent shear strengths. The same reasoning employed to explain the equivalence of the interlaminar shear strengths of the unidirectional composite specimens holds in this case; an inability of the fungi to penetrate the interfacial region to any great length during the limited exposure period may account for the lack of sensitivity of the measured shear strengths to fungal growth.

Biodegradation at Composite/Metal Joints

Documentation of Fungal Growth

Fungal growth was apparent on the composite/Al couples conditioned in malt broth after approximately five days of exposure. The specimens in salt water did not show as significant an accumulation of fungal growth. However, upon observation of the composite halves of the couples in the optical and scanning electron microscopes, fungal growth was indicated on the nonsterilized specimens. In separating the components of the couple, crystals or particles were observed to adhere to the face of the composite which was in contact with the aluminum, and an example is shown in Figure 4. Further SEM analysis using energy dispersive spectroscopy showed that the crystals contained aluminum and oxygen and, in all likelihood, are alumina peeled off from the aluminum substrate. An interesting feature in this figure is the fungal mycelia traversing the face of the crystal, suggesting that they may have penetrated and weakened the interface between the aluminum and its oxide coating thereby dislodging the crystal.

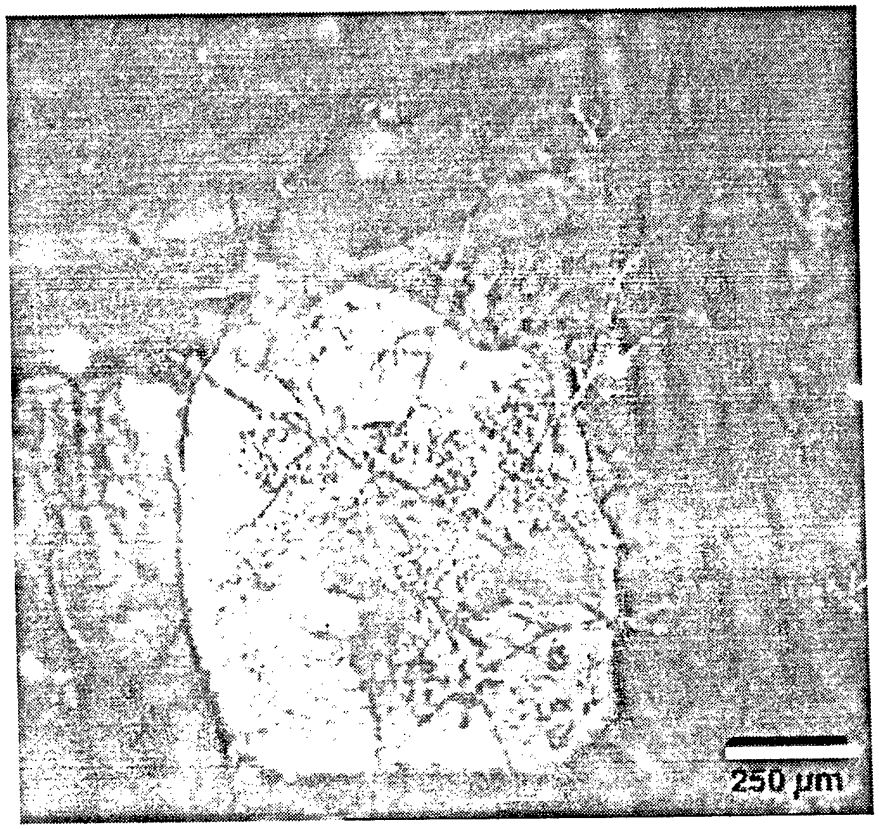

Figure 4: Fungi and crystal on BMI/Al sandwich specimen (Set J).

SUMMARY AND CONCLUSIONS

The ethylene oxide sterilization procedure appears to work fairly well at removing fungal spores from composite panels. The process did not appear to decrease the mechanical properties of the tested materials and may actually have increased the interfacial strength in some cases. Fungal growth is easily achieved on as-processed composite panels and appears within days in nutrient rich solutions. Fungal growth can also be achieved in sterilized water. Although the growth of the fungi in water is significantly less than that seen in malt broth solutions, it is apparent that nutrient rich solutions are not required for fungal development.

No significant decrease in interlaminar shear strength or interfacial strength was measured on these composites. The tests used may not have been ideal and additional testing is required to determine if the fungi are indeed degrading the mechanical integrity of either the resin, fiber, or fiber/resin interface.

The growth of fungi between composite/Al sandwiches was documented. The fungi appeared to have interacted with the surface of the aluminum and dislodged a portion of the natural Al_2O_3 coating. This could prove detrimental to the mechanical integrity of the aluminum and deserves further study.

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